

Quantum Chemical Study of Sodium Intercalation to Graphene Sandwich Structure

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Unlike lithium, sodium cannot be intercalated between graphite layers, so that the sodium ion battery with a graphite negative electrode has been considered impossible. On the other hand, in 1983, we found that the polyacenic semiconductor (PAS) as a kind of hard carbon occluded sodium and worked effectively as an electrode in an organic electrolyte cell [1,2]. Theoretical calculations showed that sodium atoms were adsorbed on the graphene surface with forming sodium clusters [3,4]. In this study, sodium intercalation to the graphene sandwich structure is investigated by quantum chemical methods to explore the occluding of sodium atoms to non-graphitizable or hard carbon.

We used large aromatic hydrocarbons such as $C_{54}H_{18}$ and $C_{96}H_{24}$ to represent a graphene sheet. Examining several kinds of stoichiometry to intercalate sodium atoms in the graphene sandwich structure, we found that the C_8Na composition was energetically preferable to the C_6Na composition. In Figure 1, the sandwich structure with the C_8Na composition was shown. For the sodium intercalation, the space between the sheets extended from the graphitic one (3.4 Å) to 4.6 Å. The extension was larger than that for the lithium intercalation by 3.9 Å. The net charge of the intercalated sodium was around 0.82; the sodium atoms were more strongly ionized than the lithium atoms by the intercalation. Occluding of sodium atoms to hard carbon materials depends on the size of the graphene sheet as well as on the structure of the surface.

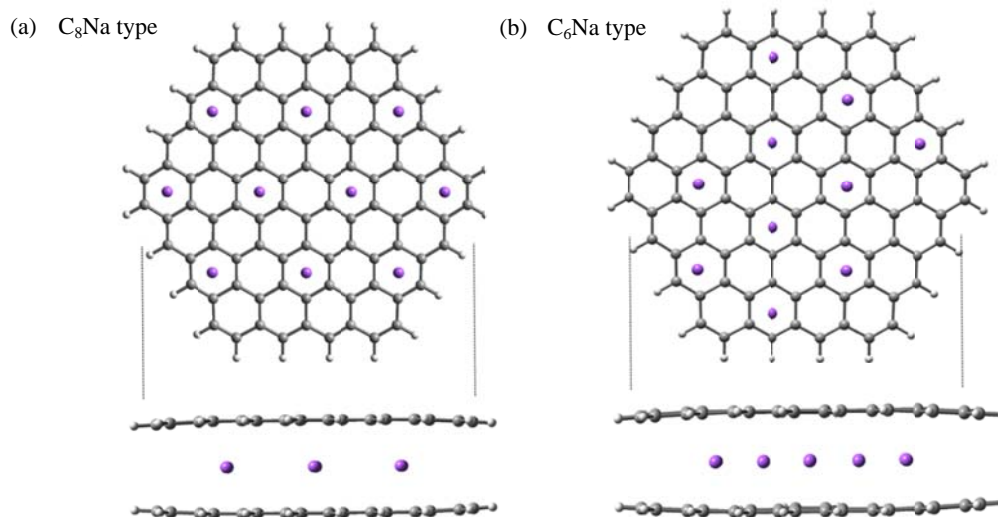


Figure 1. The optimized structure of a pair of $C_{96}H_{24}$ occluding ten Na atoms. The structures (a) and (b) represent the C_8Na and C_6Na compositions in the bulk state, respectively.

References:

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